# S&A FY03 ANNUAL REVIEW MEETING

# Solid State Sensors for Monitoring Hydrogen in IOF Process Streams

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# Project Overview

- **Project description**
  - Fabricate various Pd alloy (Au, Ni) sensor structures
  - Functionalize with inorganic coatings ($SiO_2$, SiC, SiCN)
  - Laboratory test under mixed-gas, process-like conditions
  - Field test sensors to demonstrate value added
- **Objectives**
  - Overcome limitations to existing technology
    - hydride phase transitions, aggressive chemical environments
  - Optimize alloy composition, film morphology, coating structure
- **Overall goal**
  - Develop inexpensive thin film chemical resistor technology for distributed monitoring of hydrogen in industrial process streams

# Technical Merit

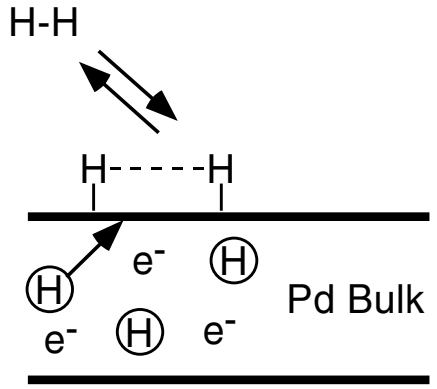
- **Measuring $H_2$ content of process streams critical to S&A community (Industries of the Future)**
  - Glass
    - surface defects in tin float baths
  - Chemicals
    - ammonia and polyolefin manufacture, batch hydrogenation
  - Petroleum
    - hydrogen recovery / cogeneration for oil refining
- **Application outside Industries of the Future**
  - Advancing the $H_2$ economy
    - generation, storage, utilization

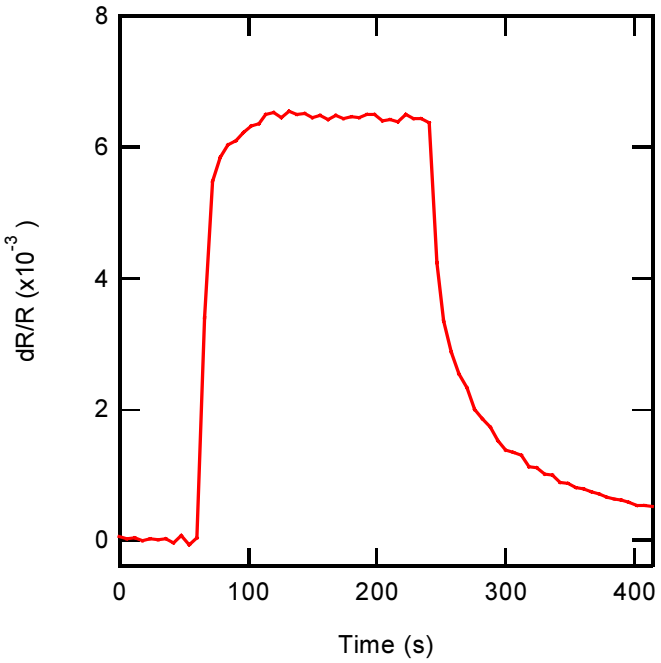
# Technical Merit

- **$H_2$ microsensor new technology to S&A community**
  - Current method
    - MS and GC/MS, complex instrument ($300K per unit)
- **Extend applicability of chemical resistor**
  - Aggressive environment
  - Mixed-gas process streams
    - $H_2$, $CH_4$, $C_2$-$C_4$ species, $H_2O$, CO, sulfur species
  - High pressure / high temperature
- **Performance metric**
  - Simple, inexpensive, robust microsensor
  - On-line hydrogen analysis time < 5 s per data point
  - Compositional analysis accuracy < 0.1% for $H_2$

# Overview of Technology

- **Thin ohmic film of transition metal alloy (Pd, Ni, Au)**
- **Principle of operation**
  - Surface chemistry moderates response
    - dissociative adsorption of $H_2$
  - Protons diffuse into bulk altering I-V characteristics
    - increase electrical resistance
    - measure change relative to nominal resistivity (dR/R)
- **Unique selectivity to $H_2$**

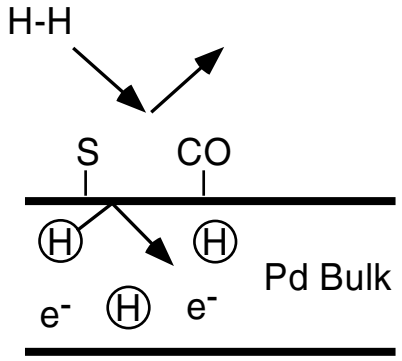


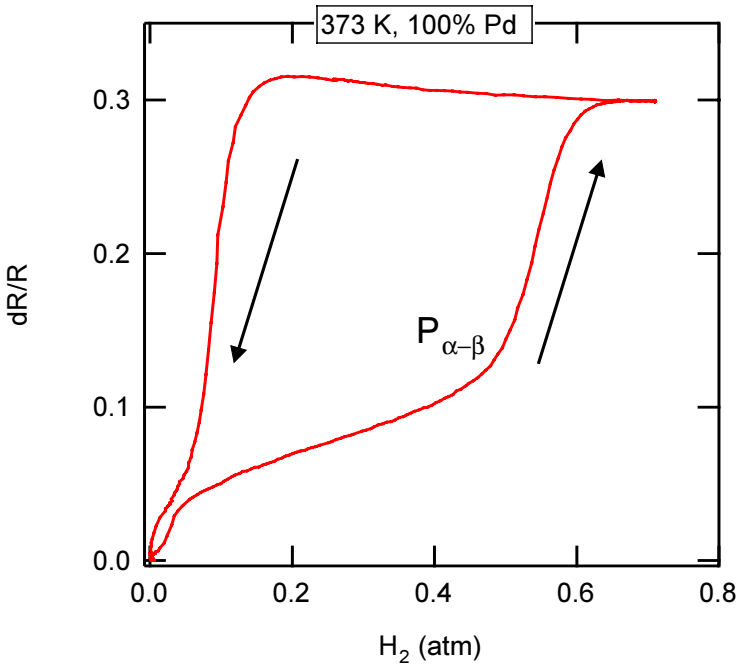



# Barriers to Industrial Applications

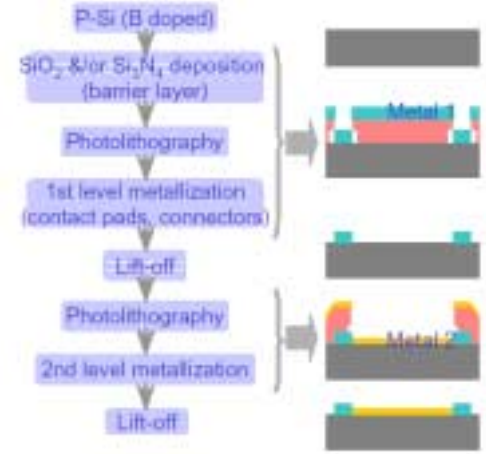
- **Hydride phase transitions at moderate $H_2$ pressures**
  - $P_{\alpha\text{-}\beta}$ < 0.6 atm $H_2$ for pure Pd
  - Increase strain in thin film
    - delaminate and destroy sensor
  - Large hysteretic effect

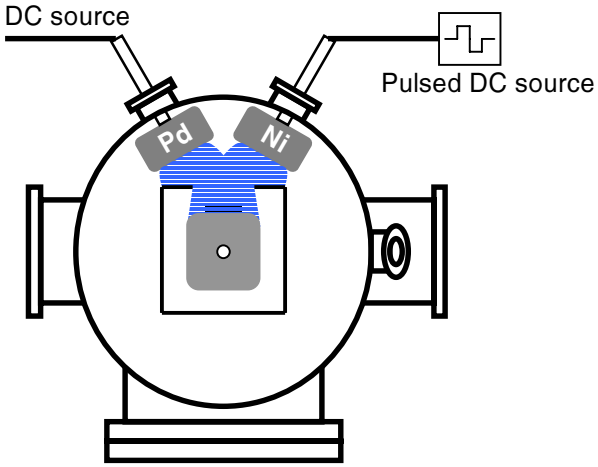
- **Poisoning of catalytic surface by CO and sulfur compounds ($H_2S$, RR'S, RHS)**

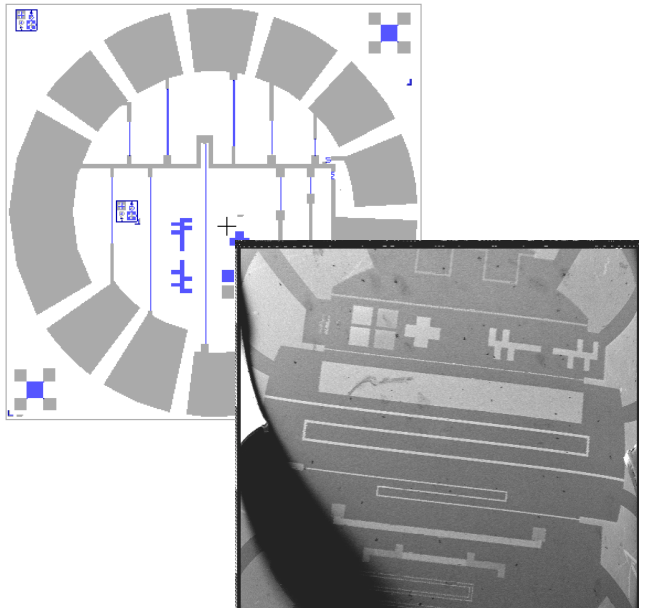


# Design, Fabricate, and Test Sensors

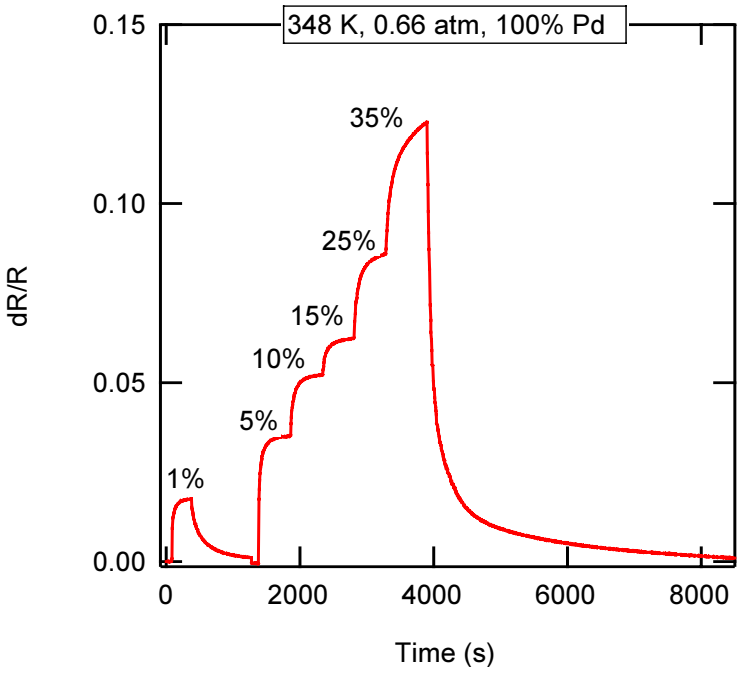


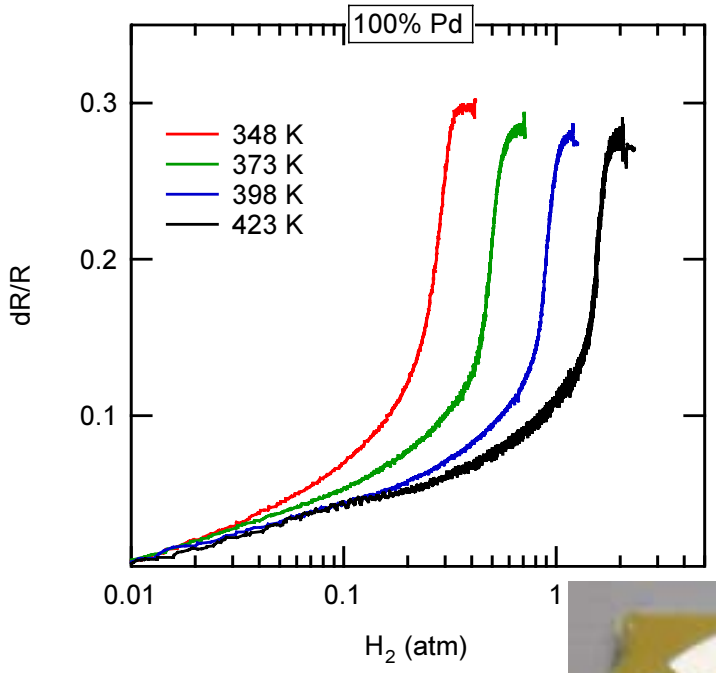



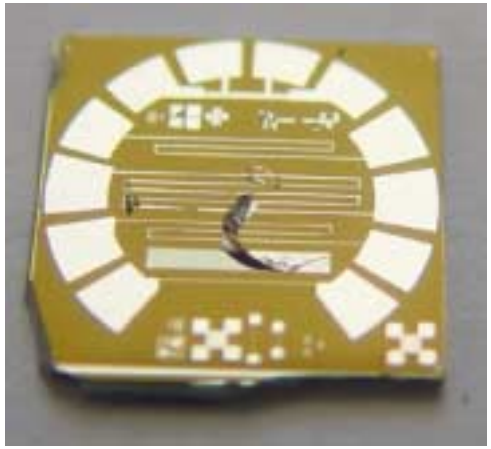



- **Microfabrication (PSU)**
  - Contact lithography, magnetron sputtering
    - precise control of film properties
- **Laboratory tests (SNL)**
  - Extensive materials evaluation capabilities
  - Flow cells with integrated diagnostics
  - Vacuum to 2000 psia

# Pure Pd Chemical Resistors

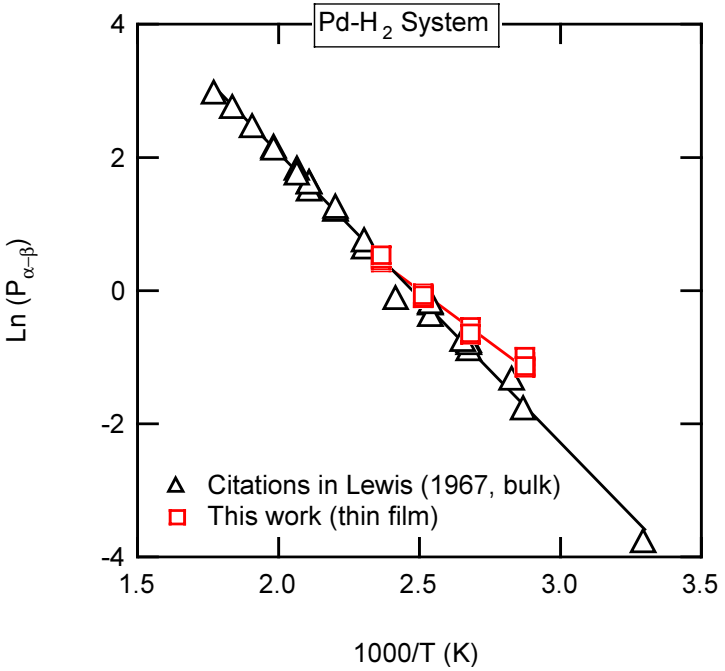


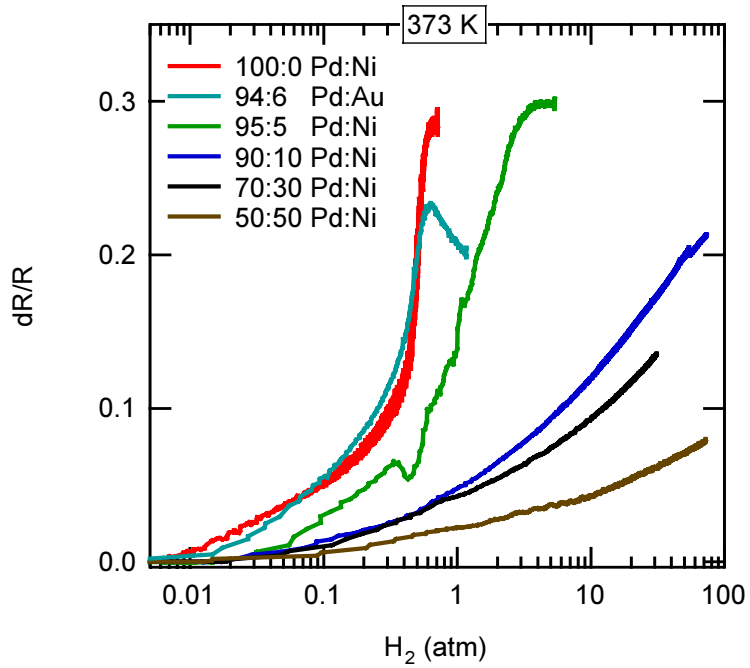



- **$H_2$ produces a change in resistance**
  - Relatively rapid response, reversible
  - Temperature dependent uptake (Sievert's Law)
- **Phase transition results in device failure**

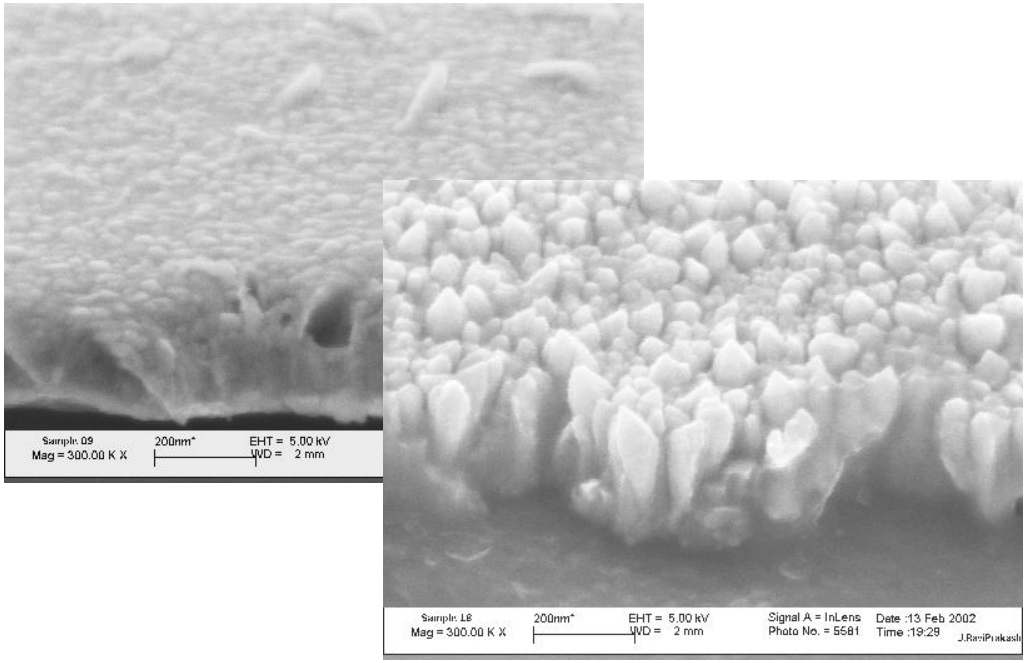
# Effects of Alloy Metal and Composition

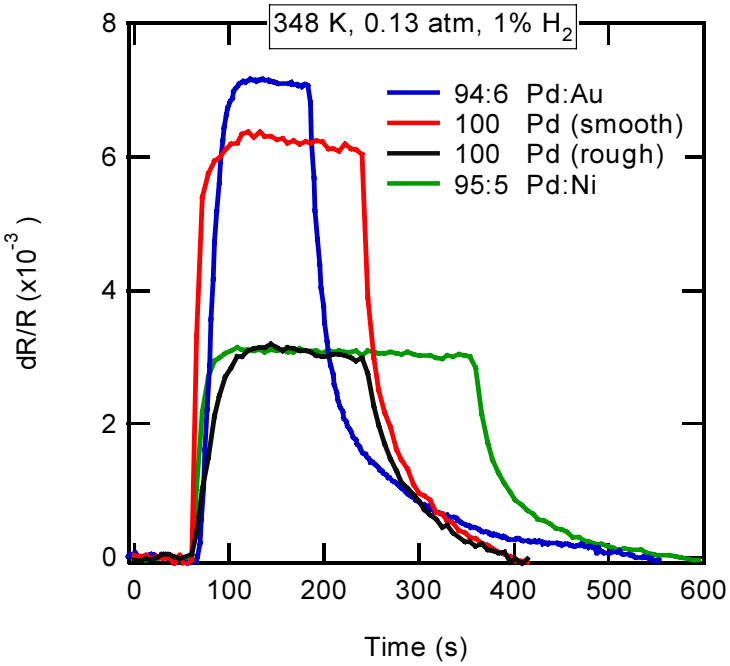



- **Thin film Pd-$H_2$ system like bulk material**
  - 1/T behavior of $P_{\alpha\text{-}\beta}$ in agreement with bulk and sintered samples
- **Alloying influences $P_{\alpha\text{-}\beta}$ hydride transition point**
  - Ni stabilizes film at the expense of sensitivity
  - Au expected to destabilize film at higher concentrations

# Effects of Film Morphology

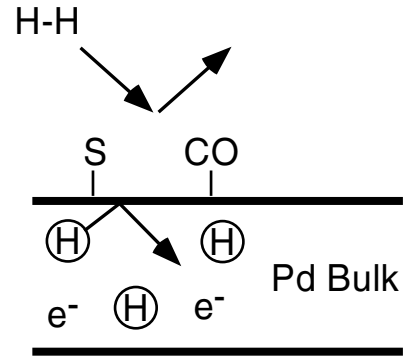


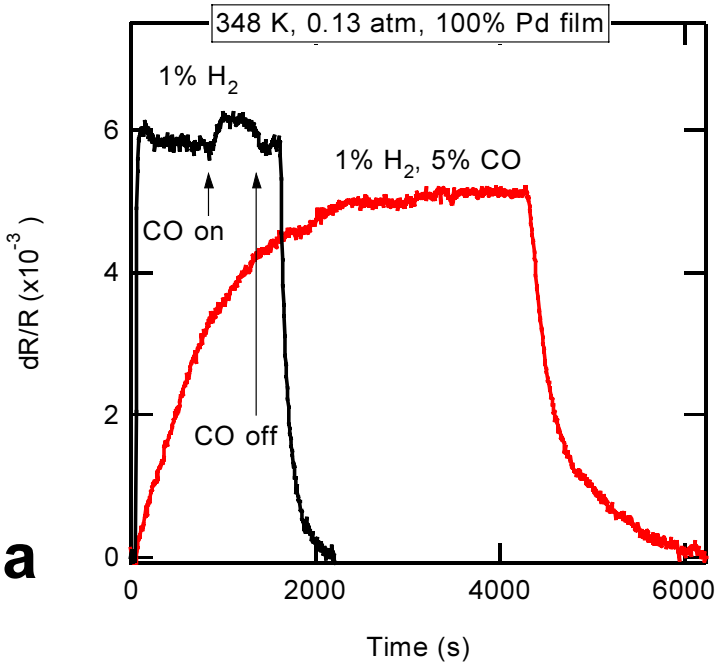




- **Alloy composition influences sensitivity**
- **Surface microstructure plays an unknown role**
  - Rough films have slower response time and lower sensitivity

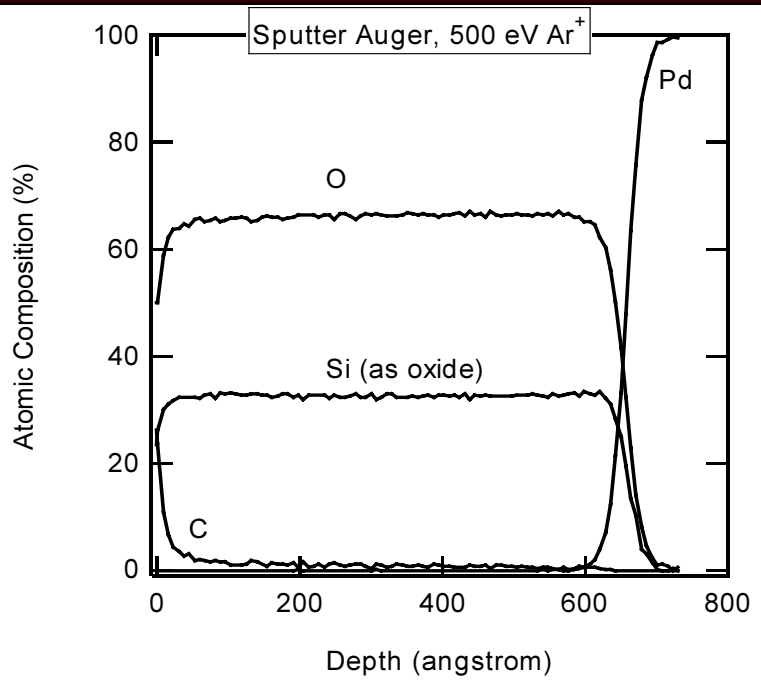
# Chemical Poisoning by CO

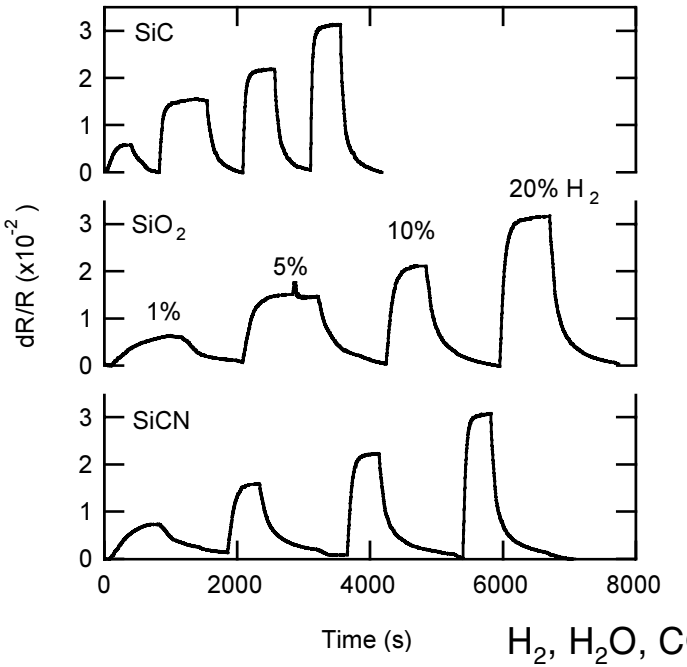
- **Surface chemistry controls response**
  - Site blocking mode
    - long response times
  - Trapping mode
    - attenuate $H_2$ sensitivity
- **Modes governed by who's first**
  - Site blocking
    - CO first, or simultaneous
  - Trapping
    - $H_2$ first
- **Kinetically controlled phenomena**

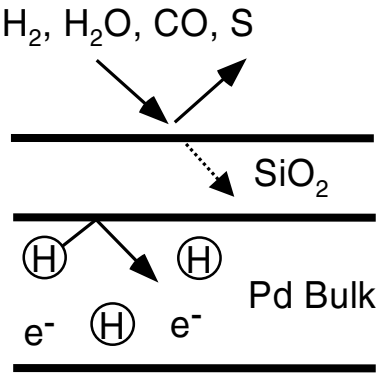


# Inorganic Films May Mitigate Poisoning

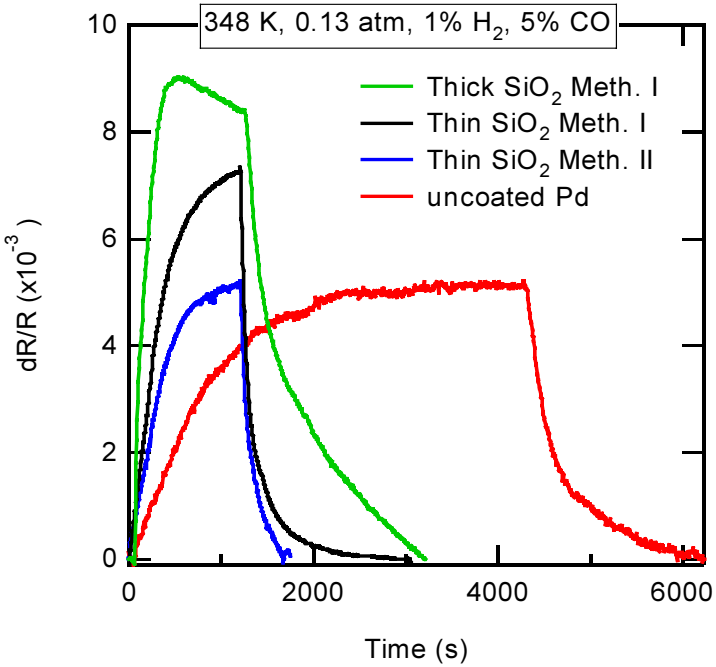


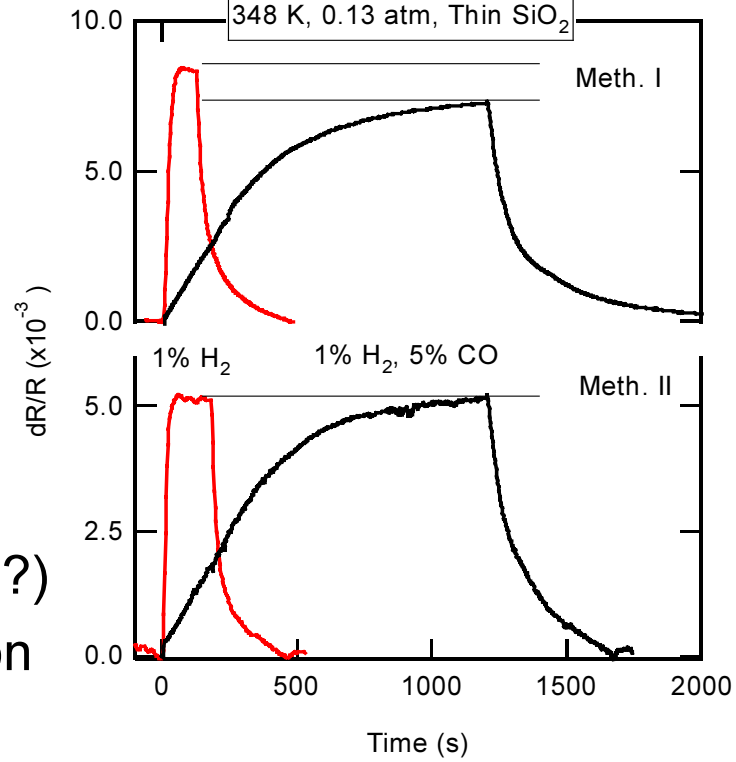




- **Thick, dense oxides, nitrides, carbides**
  - Precise control of film properties
    - composition, thickness, morphology
- **Ultimate catalyst poison!**
  - Activity at buried interface or sizeable defects in film?

# $SiO_2$ Coating - Response to $H_2$ + CO




| Sensor | 1/Response |
|---|---|
| Bare Pd | 120 |
| Thick Meth. I | 4.2 |
| Thin Meth. I | 31 |
| Thin Meth. II | 39 |




- **Clear gains in sensor response times**
  - Factor of 3 to 30 times faster (or more?)
  - May be possible to mitigate attenuation due to trapping / site blocking

# Technical Progress and Outlook

## Completed Project Milestones/Goals

| Milestone | | Due Date | Completion Date | Comments |
|---|---|---|---|---|
| PSU | Fabricate $H_2$-chemresistor test structures; vary alloy composition, incorporate membranes | 10/01<br>3/02-1/03 | 9/01<br>11/02 | completed |
| SNL | Construct laboratory testing facility | 11/00<br>1/02 | 1/01<br>4/02 | flow cell<br>high-pressure cell |
| SNL | Develop surface chemistry models for predicting sensor performance | 10/01 | 10/01 | further modeling efforts abandoned |
| SNL | Characterize sensors, determine failure modes, evaluate design changes | 1/03 | 12/02 | completed |
| DCHT | Provide equipment for field tests | 7/00<br>3/02 | 7/00<br>7/02 | business failed |
| APCI | Upgrade and prepare field unit for pilot plant testing | 2/02 | 9/02 | completed |
| APCI | Pilot plant testing | 12/00<br>7/02 | 12/00<br>4/03 | completed |

# Hydrogen Cogeneration

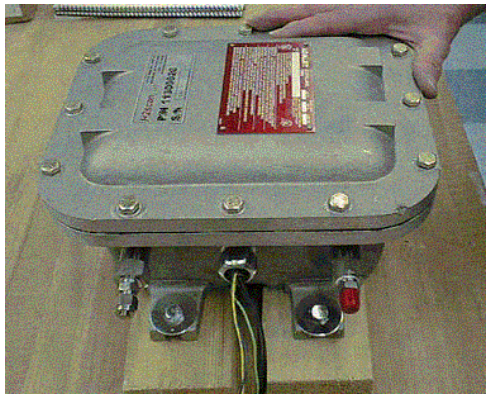
- **Air Products & Chemicals**
  - HyCO plants CA and LA
  - $H_2$ content of process streams
    - Refinery feed stock
    - Hydrocarbon reformer
    - Shift reactors (HTS,LTS)
- **Potential benefit to plant operations**
  - Redirect $H_2$-rich feed streams
  - Optimize steam-to-carbon ratio
  - Minimize gas venting
  - Reduce power consumption

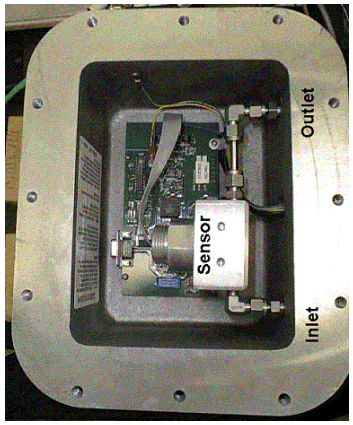
$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

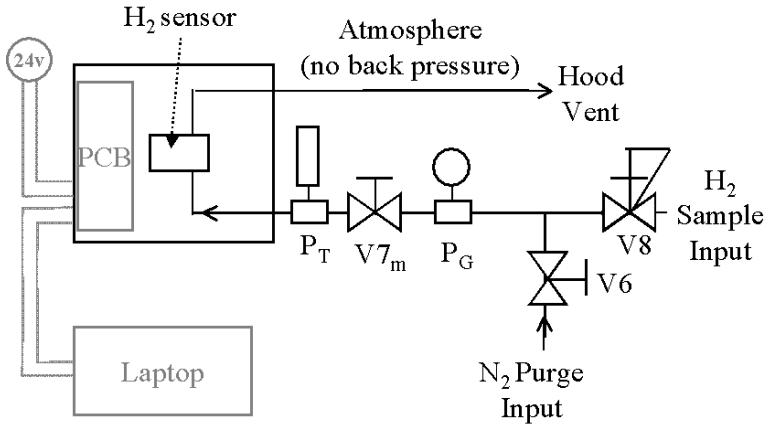
$$CO + H_2O \leftrightarrow H_2 + CO_2$$

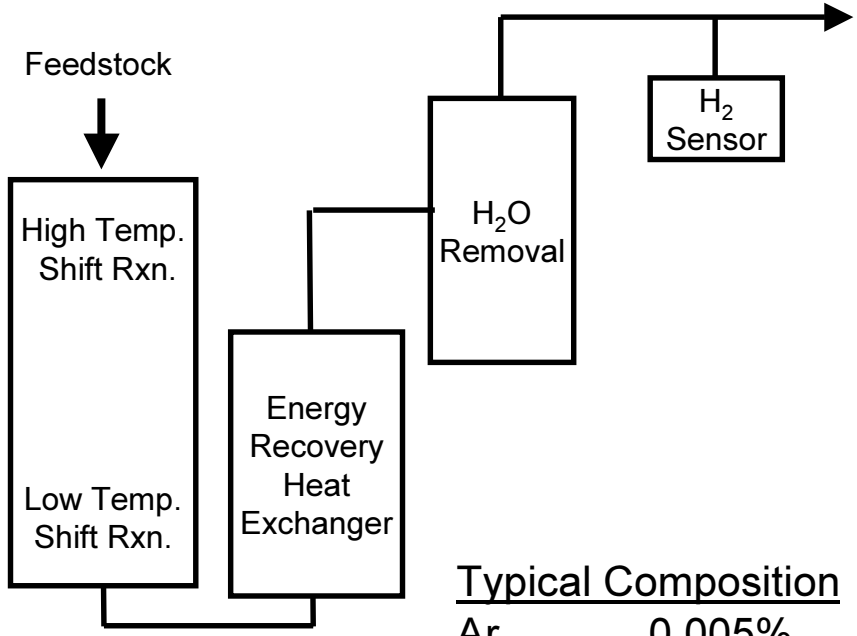
# HTS/LTS Process Measurements

## sensor





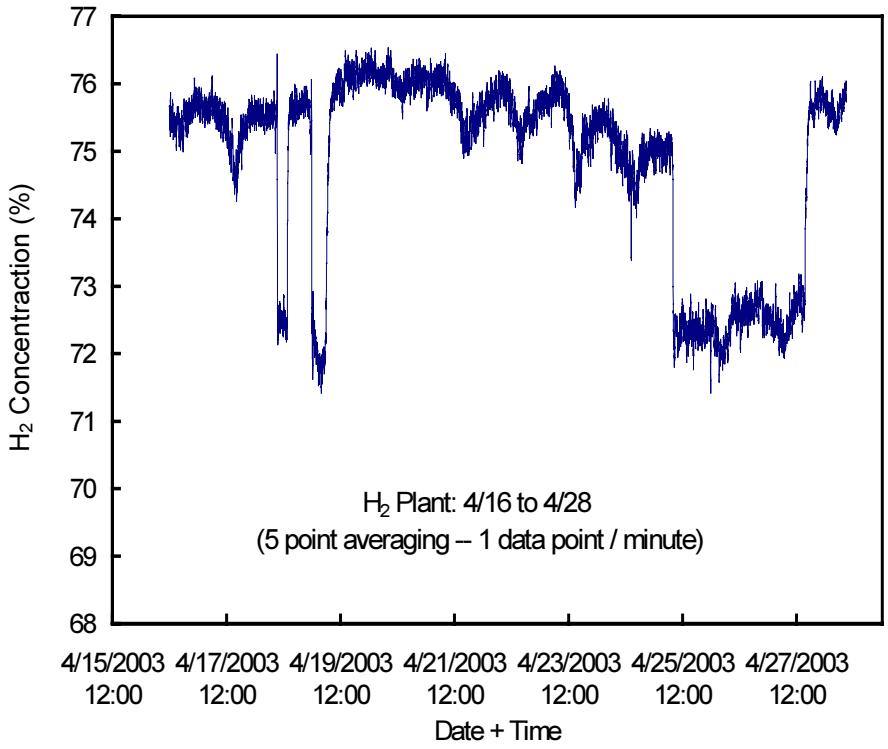

plant

**Typical Composition**

| | |
|---|---|
| Ar | 0.005% |
| $N_2$ | 0.04% |
| CO | 0.2% |
| $CH_4$ | 0.6% |
| $H_2O$ | 1.4% |
| $CO_2$ | 22.2% |
| $H_2$ | 75.6% |
| | (by difference) |

# HTS/LTS Process Measurements

- **Chemical resistor measurement in good agreement with:**
  - GC difference measurement
  - Batch sample analysis
- **Maintenance on $O_2$ feed lines showed 3% deviations in $H_2$ output**
- **Daily oscillations of $H_2$ observed for the first time**



# Market Potential

- **Major chemical and petroleum manufactures have shown interest**
  - Tennessee Eastman-Chemicals
    - batch hydrogenation
  - Air Products & Chemicals
    - hydrogen and ammonia production
  - Exxon-Mobil
  - Dow
- **Program did generate intellectual property**
  - Service and licensing responsibilities may be assumed by APCI
- **Commercialization partner DCH Technologies**
  - Identified market opportunities however company failed in 2002

# Market Potential

- **Measuring $H_2$ content of process streams critical to S&A community (Industries of the Future)**
  - Glass
    - surface defects in tin float baths
  - Chemicals
    - ammonia and polyolefin manufacture, batch hydrogenation
  - Petroleum
    - hydrogen recovery / cogeneration for oil refining
- **Application outside Industries of the Future**
  - Advancing the $H_2$ economy
    - generation, storage, utilization

# Programmatic Merit for $H_2$ Production

- **Improving energy efficiency for hydrogen cogeneration**
  - Measure $H_2$ in refinery feed and process streams
    - Redirect $H_2$-rich feed gas
    - Optimize steam-to-carbon ratio
- **Redirecting $H_2$ rich refinery feed**
  - Estimated improvement in efficiency is 0.4% per plant
    - assume 6 units installed
  - Save 1.24 BTU/SCF $H_2$ @ 0.5-1x$10^6$ SCF $H_2$/day/plant
  - Save 2.2x$10^8$ BTU/day in U.S. facilities
- **Plant optimization would yield even greater energy savings**

# Programmatic Merit for Batch Hydrogenation

- **Batch hydrogenation**
  - Monitor $H_2$ as a function of time
    - 1% improvement in sustained catalytic efficiency
    - Extend life of catalytic bed by 0.5 years
- **More than 400 hydrogenation facilities in U.S.**
    - Save \$1.5-2.5x$10^8$/year @ \$3.0-5.0x$10^5$/year/plant
    - Extending intervals between catalyst replacement could save \$2.4x$10^7$/year
- **Mass spectrometer installed cost \$3.0x$10^5$/unit**
- **$H_2$ Solid state sensor installed cost \$1.5x$10^4$/unit**
  - Chemical resistor chips are a small fraction of the installed cost!

# Summary

- **Recognized important relationships between processing and sensing environment to the application of $H_2$ chemical resistor technology**
- **Engineered solutions to barriers preventing industrial application**
  - Optimize alloy metal, composition, film morphology
  - No limit to potential coating technologies
    - inorganic, organic, combinations (sol-gels), functionalized (hydrophobic)
- **Established confidence within the industrial community by executing successful field trials**